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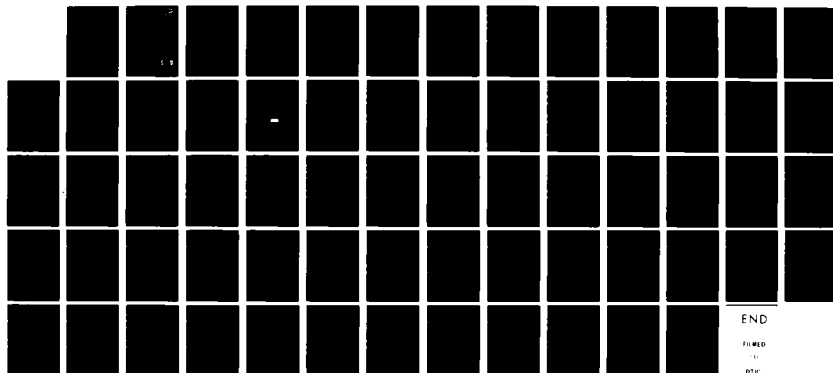
MICROBIAL FOULING AND ITS EFFECT ON POWER GENERATION
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**MICROBIAL FOULING AND ITS
EFFECT ON POWER GENERATION**

by

**W. G. Characklis
F. L. Roe
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**Second Summary Report
September, 1982**

**Prepared for M. K. Ellingsworth, Program Monitor
Power Program
The Office of Naval Research
Arlington, Virginia 22217**

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Attention has been focused on the rate of biofouling and the influence of environmental and engineering variables on this rate.

Results are also reported on preliminary experiments concerned with microbially-mediated corrosion of alloys relevant to Navy application (Cu-Ni and Ti). The combined impact of microbial fouling and corrosion poses significant shipboard problems.

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INTRODUCTION

Fouling of surfaces in marine environments is a problem which affects a wide variety of systems from ship hulls to heat exchangers. System performance, as well as operating costs, suffer due to energy losses in the form of increased fluid frictional and heat transfer resistance. Most studies to date have avoided addressing fundamental questions concerning fouling in fluid flow and heat transfer systems and their effect on fluid frictional and heat transfer resistance.

The fouling process begins with transport of materials (soluble and particulate) to a surface and their adsorption or firm adhesion to the surface. The factors which affect these processes, such as surface material, surface active films, and shear stress, determine the rate and extent of deposit accumulation during the early stages of deposit accumulation.

The initial accumulation phase is followed by a rapid, frequently logarithmic, increase in the deposit thickness and/or mass. The extent and rate of growth are moderated by factors such as water quality and shearing forces at the fluid-deposit interface. Generally, a pseudo-steady state deposit accumulation develops where loss of deposit mass to the bulk fluid (primarily due to fluid shear forces) balances production of new deposit due to physical, chemical, and/or biological processes. This report will discuss the rate and extent of accumulation of biofouling deposits, inorganic deposits, and their combination.

Resulting frictional and heat transfer resistance are closely related to specific properties of the deposit. For example, viscoelasticity and roughness of the deposit affect fluid frictional and convective heat transfer resistance, while deposit thickness and thermal conductivity influence conductive heat transfer resistance. This report will discuss the contrasting influences of fouling biofilms and inorganic scale deposits on energy losses.

Corrosion is another important deleterious effect of fouling deposits. Under-deposit corrosion is considered as one of the most serious forms of deterioration. Experimental results are reported regarding the influence of biofouling on corrosion of titanium and copper-nickel 70-30.

This report for our second funding period, 15 May 1981 through 14 May 1982, describes results of research projects related to fouling biofilm processes, the interaction between biofouling and precipitation (scaling) processes, and the interaction between biofouling and corrosion processes. The research also focused on the influence of alloys (titanium and copper-nickel 70-30) and biofouling control procedures (Cathelco and chlorine) on fouling, corrosion, and energy losses. The report is organized into the following sections:

- I. Fouling of Heat Transfer Surfaces: Analysis, Measurement, and Control**
- II. Biofouling and Corrosion**
- III. Publications and Presentations (May 1980-Sept. 1982)**

Description of methods will be minimal, limited primarily to new methods not reported in the 1980-81 annual report.

SECTION I. FOULING OF HEAT TRANSFER SURFACES: ANALYSIS, MEASUREMENT, AND CONTROL

INTRODUCTION

Fouling of heat transfer surface refers to any undesirable deposit that increases the resistance to heat transfer, increases fluid frictional resistance, and/or increases the rate of corrosion at the surface.

The general term fouling can reflect any or all of the following processes:

1. precipitation or crystallization by inorganic salts
2. sedimentation
3. corrosion
4. biofouling

Some progress is evident in the understanding of the specific types of fouling described above. However, the criticism most often directed at such research is that seldom does one specific type of fouling occur in any relevant, technical-scale application. This report will focus on the interaction between chemical, physical, and biological processes contributing to fouling deposition, measuring the deleterious effects of those deposits on heat exchanger performance, and evaluation of strategies for deposit control.

The Problem

The electric power and chemical process industries use a large amount of cooling water, comprising 1/3 of all water consumption in the United States [1]. Cooling water contains an endless variety of "impurities" which may lead to the formation of a fouling deposit including the following: dissolved organics and inorganics, particulates, and microorganisms. The fouling deposits are major causes of energy losses in the electric power industry, chemical process industry, and for the Navy. In fact, fouling has been referred to as the "major unresolved problem" in heat transfer [2,3]. Lund [4] estimates the annual fouling cost to the United States in 1980 at \$1.8-2.9 billion. These costs include increased capital costs for added heat transfer surface, energy losses, maintenance costs, and loss of production. Others have also estimated the dramatically high costs of fouling [5,6,7].

Generally, fouling is accounted for in engineering design of heat exchangers by adding extra surface area (i.e., fouling resistance) in addition to the "clean design area." The values for fouling resistance are selected from tables containing data of questionable accuracy and frequently obtained from unidentified sources. The extra surface area frequently is more than half of the total heat exchanger area and accounts for a significant fraction of the exchanger cost. Moreover, selection of a high fouling resistance does not guarantee prolonged operation of the heat exchanger. This design procedure also increases the size and weight of the exchanger unnecessarily, a problem of major concern to the Navy.

Present Control Techniques

Many techniques have been proposed to remedy the problems of fouling including chemical treatment, physical treatment, enhanced heat transfer surfaces, and various types of coatings. The choice of treatment and/or control technique depends on the type of fouling deposit (Table I-1) but many of the techniques remain to be tested in an effective manner. In some cases, treatment for one type of fouling deposit may be ineffective in the presence of another type of fouling. For example, addition of inhibitors to prevent scale formation (e.g., phosphonates) may prove futile in the presence of biofouling activity. Therefore, the composition of the fouling deposit determines the proper treatment.

Table I-1. Fouling Treatment and Control

	Scaling	Biofouling
External Treatment	softening ion exchange	
Internal Treatment	pH control softening acid feed side stream treatment flocculants dispersants surfactants chelants	pH control oxidizing biocides — chlorine — ozone — bromine — hydrogen-peroxide non-oxidizing biocides — chlorinated phenolics — organo-tin compounds — quaternary ammonium salts — surfactants
Removal	mechanical cleaning acid treatment	mechanical cleaning oxidizing biocides

Monitoring Fouling Deposition

Traditionally, water quality parameters (e.g., hardness, alkalinity, bacterial counts) have been used to predict fouling potential and determine the type treatment. But these parameters define conditions in the bulk water which generally are significantly different from surface conditions where the problem exists. More recently, fouling monitors have been developed which indicate the effects of a fouling deposit on fluid frictional resistance and heat transfer resistance. These measurements yield no information regarding the composition of the deposit.

Recent experiments in our laboratory suggest that a fouling monitor can be used to discriminate *in situ* between different types of fouling deposits on the basis of their thermal conductivity and roughness [8]. Tables I-2 and I-3 compare experimentally determined properties for a biofouling deposit, a scale, and a combined biofouling/scale deposit. *In situ* diagnostic measurements of this type could serve as decision variables for internal control of fouling.

Table I-2. Thermal Conductivity of Various Deposits

Type Deposit	Thermal Conductivity (watt m ⁻¹ C ⁻¹)
Biofilm	0.63
Calcium Carbonate	2.26-2.93
Combined Biofilm/Scale	1.61

Table I-3. Roughness Characteristics of Various Deposits

Type Deposit	Deposit Thickness (cm)	Relative Roughness (dimensionless)
Biofilms	0.0040	0.003
	0.0165	0.014
	0.0300	0.062
	0.0500	0.157
CaCO ₃ Scale	0.0165	0.0001
	0.0224	0.0002
	0.0262	0.0006
Combined Biofilm/Scale	0.0118	0.006
	0.0363	0.04

This research has focused on the fundamental causes of fouling of heat exchange surfaces, its prediction, detection, diagnosis, and amelioration.

BACKGROUND

Fouling of heat transfer surfaces on the cooling water side of a heat exchanger/condenser can be classified into four main categories: (1) biofouling, (2) scaling or precipitation fouling, (3) corrosion, and (4) sedimentation.

Biofouling is a general term referring to undesirable effects due to attachment of microorganisms. The attached microorganisms produce an extracellular polymer substance (EPS) which results in a slime layer [9,10,11] on the inside of water conduits/tubes causing increased frictional resistance and energy losses. Characklis [12,13,14] and Norrman *et al.* [15] have reviewed the literature concerning biofilm development and its effect on frictional resistance.

Scaling or precipitation fouling is primarily due to precipitation of calcium salts on heated surfaces. The potential for scaling is greatest in water having increased hardness or total dissolved solids. Taborek *et al.* [2,3], Knudsen *et al.* [16,17,18,19], and Hasson [20] have

reviewed the literature and the factors concerning scale deposition and its influence on heat transfer resistance. Other literature concerning scaling can be found elsewhere [1,5,7,40,41].

Deposition of organic and inorganic substances on a heat transfer surface may increase the corrosion rate at the surface. Corrosion can be defined as an electrochemical process whereby part of the surface is oxidized and transferred from the solid state into solution, accompanied by simultaneous reduction of some component in the corrosive environment. Literature related to corrosion due to microbial fouling and the factors affecting corrosion processes can be found elsewhere [5,7,44,45,58-61]. Recent work completed in our laboratory considered the effects of biofouling on corrosion processes and their combined influence on energy losses (Section II).

Biofilm Processes

Biofilm development is the net result of physical transport and biochemical conversions. The following processes contribute to overall biofilm accumulation [21,22]:

- organic adsorption at the wetted surface
- transport of the microbial particles to the surface
- microorganism attachment to the surface
- growth and other metabolic processes by the attached microorganisms
- reentrainment of biofilm by fluid shear forces

Organic adsorption. Attached microorganisms select their habitats on the basis of many factors [23-26] including the nature of the wetted surface (material of construction and surface roughness).

Figure I-1 illustrates an initially "clean" surface exposed to turbulent flow of a fluid containing dispersed microorganisms, nutrient, and organic macromolecules. Adsorption of an organic monolayer occurs within minutes of exposure. Investigations have shown that materials with diverse surface properties (e.g., wettability, surface tension, electrophoretic mobility) are rapidly conditioned by adsorbing organics once exposed to natural waters with low organic concentrations [26,27].

Transport of microbial particles to the surface. Figure I-1 indicates the physical transport of particles from the bulk fluid to the surface covered by an organic film. Within a turbulent flow regimes, particles suspended in the fluid are subjected to several forces as they move towards the solid surfaces. Theory indicates that the flux of particles to the surface increases with increasing fluid velocity and particle concentration. However, particle flux is strongly dependent on the physical properties of the particles (e.g., size, shape, density) and the fluid [28,29].

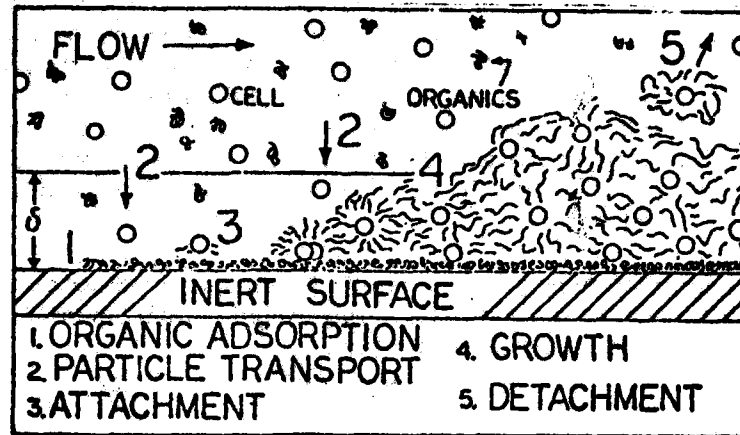


Figure I-1. Summary diagram of biofouling processes.

Microorganisms attachment to the surface. Research suggests the existence of a two-stage attachment process [25,26,30]: reversible attachment followed by an irreversible adhesion. Reversible attachment refers to an initially weak adhesion of a bacterium to a surface. Organisms still exhibit Brownian motion and are readily removed by mild rinsing. Conversely, irreversible adhesion refers to a strong adhesion to the surface, usually aided by the production of cellular exopolymers. Irreversibly attached bacteria can only be removed severe physical or chemical treatment.

Previous studies of microbial cell attachment have been conducted at very low fluid shear rates or under quiescent conditions. Rates of accumulation determined from these studies are very likely mass transfer-limited (i.e., diffusion-limited or sedimentation-limited) and not necessarily applicable to environments where fluid shear rates are quite high.

Metabolism by attached microorganisms. Once attached to the surface, the organisms assimilate nutrients and synthesize new cellular and extracellular material which accumulates in the surface deposit. The rate of biofilm production due to nutrient assimilation has been experimentally observed in our laboratory as functions of nutrient concentration, fluid velocity, and temperature [31-34]. Postulated rate expression for nutrient depletion by a biofilm are numerous and consider the effects of nutrient diffusion and depletion in the biofilm [31-38]. The postulated rate expression can be generally classified in two categories: (1) structured models which have not been experimentally verified and (2) unstructured or "curve fit" models developed from experimental data obtained with undefined mixed microbial populations. However, only two of these models relate nutrient depletion rate processes to biofilm product formation processes [33,34]. Results indicate high biomass yields during the initial stage of biofilm development with high concentrations of EPS present in the biofilm. Yield steadily decreases during development to relatively low levels suggesting high maintenance energy requirement or biomass decay in the deeper layers of the film.

Detachment of biofilm by fluid shear stress. At any point in the development of biofilm, portions of biofilm detach from the surface and are reentrained in the bulk flow. Detachment is a continuous process of biofilm removal and is highly dependent on hydrodynamic conditions [32]. Sloughing, on the other hand, appears to be a random, massive removal of biofilm attributed to oxygen/nutrient depletion deep within the biofilms [39]. Sloughing is more frequently witnessed with thicker, dense films especially in laminar flow. More work is needed to quantify either effect.

In summary, biofouling is the net result of these rate processes occurring simultaneously (Figure I-1). However, at specific times during overall biofilm development, certain processes may contribute more significantly than others.

Scale Deposit Mechanism

The formation of mineral scale on heat transfer surfaces is due to deposition of salts having inverse solubility characteristics. When the solubility product of such material is exceeded, it precipitates and forms scale. Cowan and Weintritt [41] have analyzed the controlling parameters affecting the overall scaling process. Figure I-2 is a general schematic diagram of the scale deposition mechanism. There are several processes [41] that influence the formation of the initial scale layer and its subsequent growth. These include nucleation, diffusion, chemical reaction, and molecular reordering of the crystal lattice.

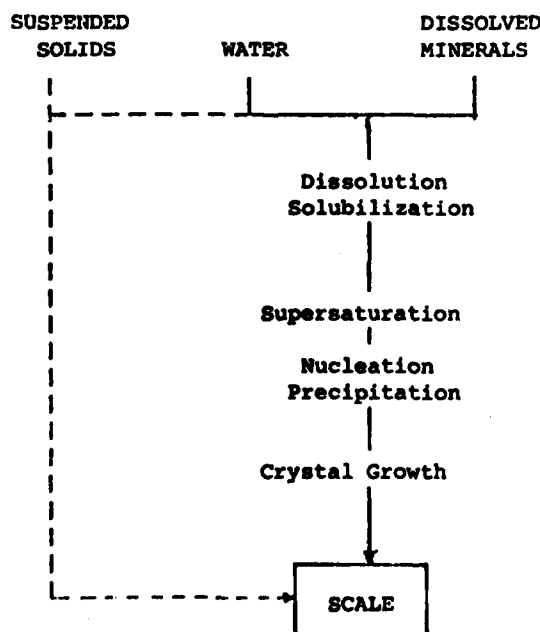


Figure I-2. General schematic diagram of scale deposition mechanism (from Cowan and Weintritt).

Cooling water contains a large number of potential scale and deposit-causing constituents such as calcium, magnesium, and iron salts that will precipitate as a result of changes in temperature, pH, concentration, and incompatible additives. Such deposits commonly contain constituents such as calcium carbonate, calcium sulfate, calcium phosphate, magnesium salts, iron hydroxide and sulfides, and organic constituents. According to York and Schorle [42], there are three simultaneous factors that influence crystallization of a salt directly on-site of scale formation. These include supersaturation, nucleation, and adequate contact time. Among other factors which affect the formation of scale deposits, alteration in pH is of particular importance and affects the deposition of scale such as calcium carbonate, magnesium hydroxide, and iron compounds. An increase in pH generally tends to precipitate such compounds while decrease in pH tends to keep potential scale-forming material in solution.

Mathematical Simulation of Biofilm Inside a Circular Tube

A mathematical model simulating fouling biofilm development and its influence on heat transfer may be useful for several purposes including the following (after Himmelblau and Bischoff [43]):

Economical experimentation – fouling processes can be studied more quickly and economically than possible in the laboratory or field.

Extrapolation – extreme ranges of operating conditions can be tested which may be impractical otherwise.

Evaluation of alternative policies – various designs, operating procedures, and treatment processes can be tested before decisions are made.

Design of experiments – the model can indicate the variable to be measured and the data that must be provided for useful evaluation procedures in the field.

Test of sensitivity – the model can indicate which parameters have a significant influence on process behavior.

However, one significant limitation of modelling must be recognized. The success of the model depends on the basic information available. The model is only as accurate as the physical, chemical, and biological data that go into the model.

A model describing biofilm development in a circular tube and its influence on overall heat transfer resistance has been developed in our laboratory. A summary flow diagram of the model is shown in Figure I-3 and the detailed description of the model is presented elsewhere [50].

Effects of Fouling

Fouling deposits can cause the following deleterious effects in heat exchangers:

- increased fluid friction resistance
- increased overall heat transfer resistance
- increased corrosion rate

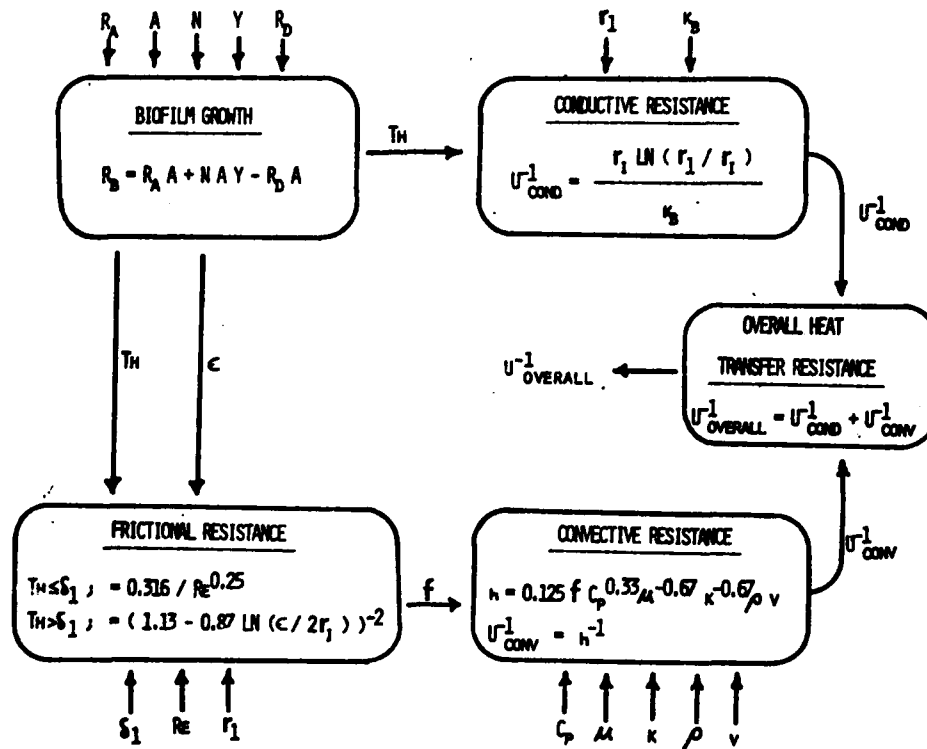


Figure I-3. Biofilm development and heat transfer resistance model.

Frictional resistance. Fouling deposits cause increased frictional resistance by decreasing the effective diameter of the heat exchanger tube and by increasing the tube roughness. Figure I-4 shows the increase of pressure drop and biofilm thickness with time due to biofilm accumulation in a constant flow rate experiment. The energy loss, indicated by increased pressure drop, results in an increased power requirement for pumping. Frictional resistance due to fouling has also been observed in the field. These losses are of major concern in water supply distribution, power generation, and wastewater collection systems.

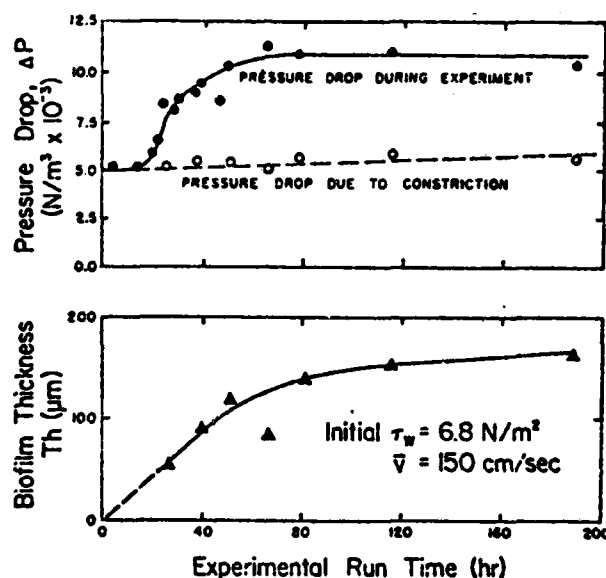


Figure I-4. Progression of pressure drop and biofilm thickness with time in a constant flow rate experiment.

Picologlou *et al.* [46] have shown *tube constriction* to be an insignificant cause of frictional resistance resulting from biofilm formation (Figure I-4). In contrast, constriction of tubing by scale deposits has been shown to be substantial [41]. Scale, a relatively rigid rough surface, affects frictional resistance differently than biofilms and is characterized by a low relative roughness (Table I-3).

Overall heat transfer resistance. Overall heat transfer resistance is the sum of conductive and convective resistances. Convective heat transfer will decrease as fouling progress due to increased turbulence resulting from deposit formation. Conductive heat transfer resistance will increase as the insulating fouling deposit accumulates. The relative contribution of convective and conductive resistance to overall heat transfer resistance due to biofilm deposition in a laboratory experiment [48,51] is shown in Figure I-5. The low convective resistance is due

to pronounced relative roughness of the biofilm which causes increased turbulence. Recent experiments in our laboratory indicate relative roughness of calcium carbonate scale deposit is small as compared to that of biofilms (Table I-3) resulting in negligible changes in convective heat transfer resistance.

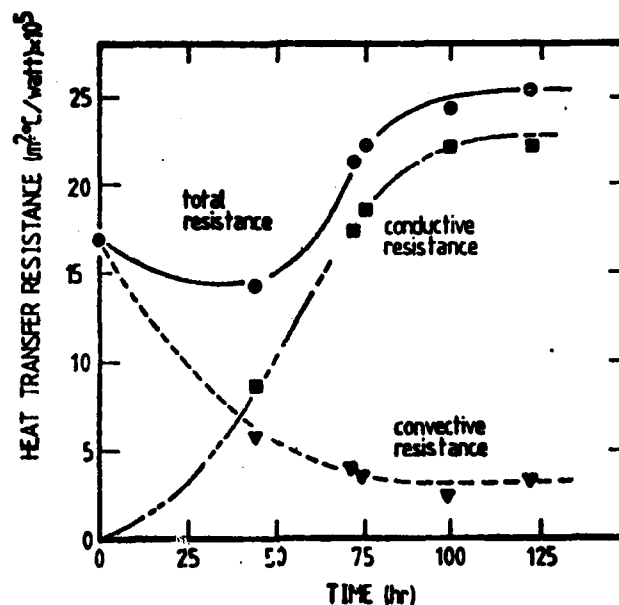


Figure I-5. Relative contribution of convective and conductive resistance to overall HTR due to biofilm deposition.

Corrosion. Corrosion in heat exchange equipment can result in:

- loss of material which could lead to the failure of that surface
- the deposition of corrosion products on heat transfer surfaces

The corrosion products deposited on heat transfer surface increase resistance to heat transfer and fluid flow. These losses are of major concern in the power and chemical process industries. Somerscales [7] describes the corrosion-related fouling phenomena as *ex situ* and *in situ* corrosion fouling. Literature related to the influence of corrosion fouling on heat transfer resistance can be found elsewhere [62-68].

ONGOING RESEARCH

Over the past four years, our research team has been conducting biofouling research. The investigations stem from the apparent need for a more fundamental understanding of biofilm development and biofilm destruction so that the impact of equipment design and operating procedures, as well as environmental regulation, can be evaluated. Results obtained

in our laboratory indicate that nutrient concentration, fluid shear stress, and temperature can influence the various processes which contribute to biofilm development. Fluid shear stress also influences the effectiveness of chlorine in destroying biofilm. Repeated chlorination results in the accumulation of the deposit, inorganic and organic, which enhances rapid recolonization of the surface.

Presently, research is being conducted for the Office of Naval Research to evaluate the effect of surface material (metallurgy) and fouling treatments on both biological fouling and corrosion fouling of shipboard heat exchangers. Closed looped systems of heat exchanger tubing has been built in the laboratory to simulate full scale systems. The tubing is interchangeable so that various metals can be tested, in these test fouling on titanium is compared to fouling on 70:30 Cu/Ni tubing. Treatment by chlorine and Cathelco method are being compared on both types of metal surfaces.

METHODS

Two reactor geometries have been used with success in our laboratory:

- circular tube (tubular fouling monitor)
- rotating annulus (annular fouling monitor)

Tubular fouling monitor. The tubular fouling monitor (TFM) is described schematically in Figure I-6. Its advantages include the following:

- can measure display and store the rate and extent of fouling in terms of frictional resistance and overall heat transfer resistance
- can control heat flux or surface temperature to simulate plant conditions
- can control pressure drop or fluid velocity to simulate plant conditions
- tube material is easily interchangeable
- can be used to study/monitor biofouling, corrosion, scaling, and/or interaction between different types of deposits

The tubular fouling monitor [50,52] consists of the following major components (Figure I-7):

1. A *heat transfer section* consisting of an electrically heated metal block clamped around a tube. Two thermistors are embedded in the metal block (TWHE) at two different radial distances from the center of the tube. The tube is interchangeable and can be made of any alloy. The tube contains ports for pressure drop measurement. The pressure drop across the TWHE is measured by a differential pressure transducer. The monitor also includes a flow meter and two temperature probes for bulk water temperature.

2. An *Apple II plus* microcomputer serves as a complete data processing system. From the data (flow, pressure drop, and temperatures), friction factor, convective heat transfer resistance (HTR), conductive HTR, and overall HTR are calculated. The microcomputer can also *control* the following:

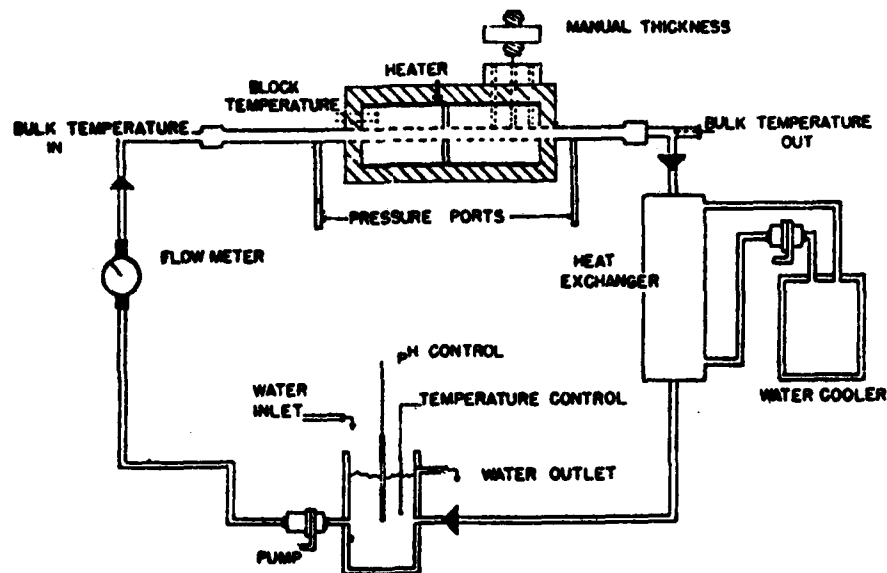


Figure I-6. Simplified flow diagram of the experimental system.

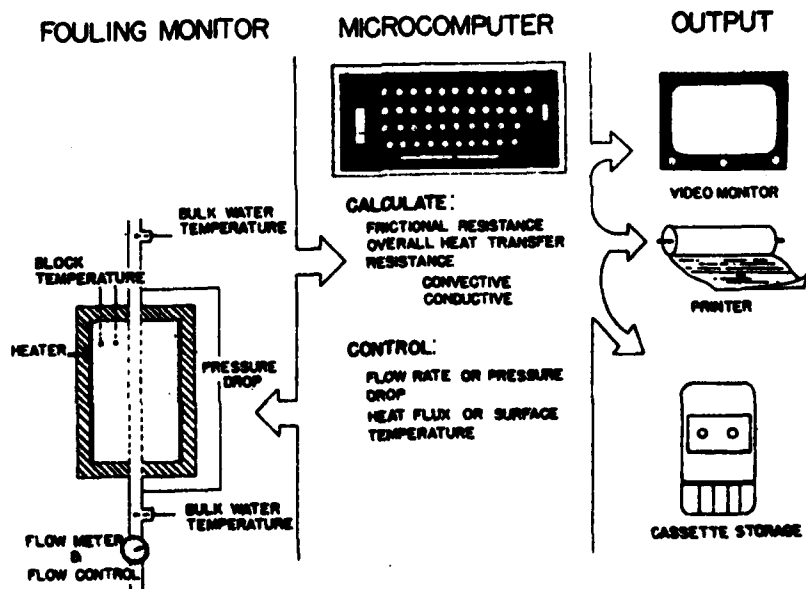


Figure I-7. Fouling monitoring system.

pressure drop or flow rate
heat flux or inside wall temperature

Output from the microcomputer includes a CRT (television) monitor for instantaneous display and a cassette recorder or disk for data storage.

3. A *test section* consists of a series of 5 cm long removable sample tubes which are held in place to form a continuous tube. The sample tube may be removed for:

- Estimating deposit volume, mass, and thickness
- Microbial Analysis (e.g., viable and total cell counts)
- Inorganic Analysis
- Scanning Electron Microscopy
- Visual Observations

The test section is placed in a recirculating hot water bath. The temperature of the bath can be adjusted to match the wall temperature of the tube in the heat transfer section.

Annual fouling monitor (AFM). The AFM essentially consists of two (acrylic) concentric cylinders, a stationary outer cylinder and a rotating inner cylinder. A torque transducer mounted on the shaft of the reactor between the rotating cylinder and the motor drive continuously monitors changes in fluid friction resistance. A detailed description of this type of reactor is presented elsewhere [22].

Fouling Measurement Techniques

Fouling in the laboratory reactor system (TFM) described earlier is measured by monitoring the changes in the following parameters:

1. overall heat transfer resistance
2. frictional resistance
3. deposit thickness

The first two methods are the effect of deposition while the latter is a direct measure of the deposit accumulation.

Overall heat transfer resistance. Figure 1-8 is a schematic cross-sectional diagram of the heat transfer section heated at a constant rate. The overall heat transfer resistance (based on average bulk water temperature) can be obtained:

$$U^{-1} = \frac{2\pi r_i l (T_i - T_{B(avg)})}{q} \quad (1)$$

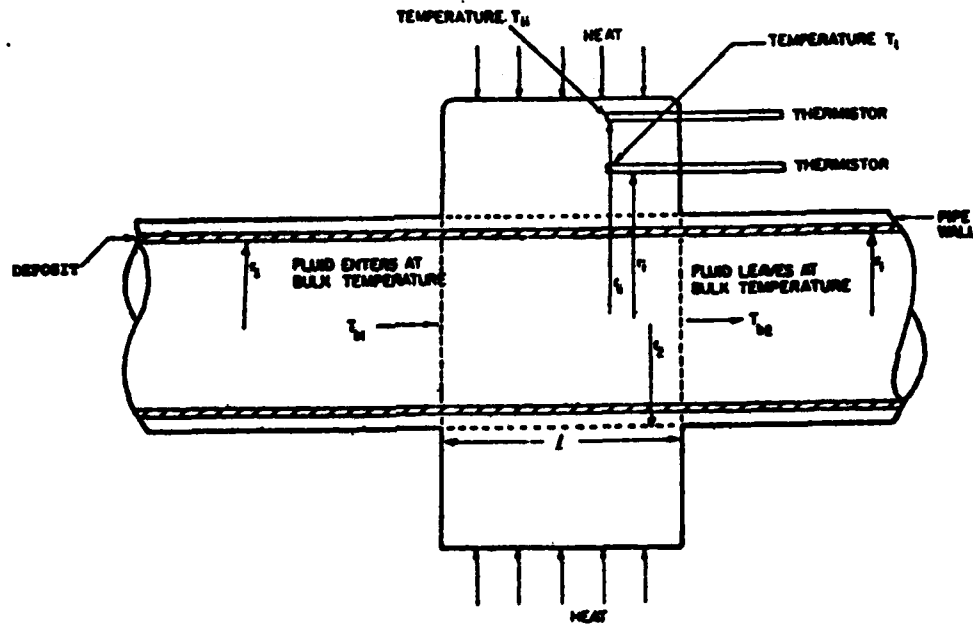


Figure I-8. Schematic cross sectional diagram of TWHE.

The overall heat transfer resistance is the sum of conductive and convective resistance and is given by:

$$U^{-1} = \frac{r_1}{r_1 h} + \frac{r_1 \ln(r_1/r_1)}{k_D} + \frac{r_1 \ln(r_2/r_1)}{k_T} + \frac{r_1 \ln(r_1/r_2)}{k_M} \quad (2)$$

convective
resistance

conductive resistance

The convective heat transfer resistance can be calculated using the Colburn analogy [49]. Equation (2) can be used to calculate the thermal conductivity of the deposit provided the thickness of the deposit is known/measured. The influence of the deposit on heat transfer resistance can also be expressed more traditionally as follows:

- (a) Fouling resistance [55]
- (b) Performance index [56]

Frictional resistance. Fouling deposits can cause increased fluid friction resistance by decreasing the effective diameter of the tube and increasing the tube roughness. Frictional resistance is determined from the pressure drop and flow measurement in the heat transfer section and is calculated by [46]:

$$f = \frac{4 r_1 \Delta P}{L \rho_f v^3} \quad (3)$$

Deposit thickness. The thickness of the deposit in the test section is estimated from the volume of the deposit. A detailed description of the method for estimating the deposit volume is presented elsewhere [38]. Deposit thickness is determined by dividing deposit volume by the surface area of the tube.

Influence of Organic/Inorganic Deposits on Heat Transfer Resistance: Preliminary Studies

Experiments have been conducted in our laboratory to determine the influence of different types of deposit on heat transfer resistance. In this study, the tube alloy (70:30 Cu/Ni), bulk water temperature (35 C), flow velocity (0.91 m s⁻¹ or 3 fps), calcium content (250 mg l⁻¹), and the pH of the water (8-8.2) were held constant in all the experiments. The influence of three different types of deposit on heat transfer resistance was determined.

In the case of a combined biofilm/scale, the experiment was initiated by inoculating the fermenter with a mixed population of microorganisms and operating in the batch mode for 8-10 hours. The system was then continuously supplied with 5 mg l⁻¹ glucose. In the case of silicate scale, the system was continuously supplied with 200 mg l⁻¹ of sodium silicate while in the case of a pure calcium carbonate scale the system was not supplied with glucose or sodium silicate. The following observations were noteworthy:

1. Different types of deposit were found to exhibit a different rate and extent of fouling as measured by the increase in overall heat transfer resistance
2. In the case of "pure scale" (Figure I-9), the increase in overall heat transfer resistance was largely due to the increase in conductive resistance. This type of deposit was found to exhibit a low relative roughness and the convective resistance was essentially constant.
3. The calcium carbonate/silicate scale (Figure I-10) exhibited a higher increase in overall heat transfer resistance as compared to a calcium carbonate scale
4. For the combined biofilm/scale (Figure I-11), the increase in conductive resistance of the deposit was largely offset by the decrease in convective resistance (due to deposit roughness).

It is customary to report fouling data in terms of "fouling resistance," R_f [5,7,16-20]. These experiments indicate that "fouling resistance" *does not* yield any valuable diagnostic information if the deposit is either a pure biofilm or a combined/scale (Figure I-11). At an asymptotic fouling resistance, an increase in thickness was observed. This increase in conductive resistance (due to deposit thickness) was largely offset by the decrease in convective resistance of the deposit and, hence, the fouling resistance essentially remained constant.

However, frictional resistance measurements, in conjunction with heat transfer measurements, can yield valuable information on the progress of fouling and the type of fouling deposit.

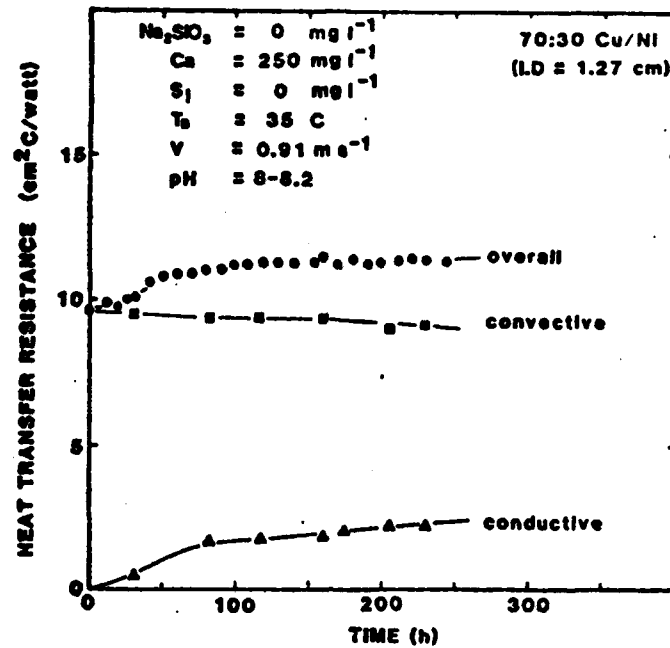


Figure I-9. Relative contribution of convective and conductive resistance to overall HTR due to deposition of calcium carbonate.

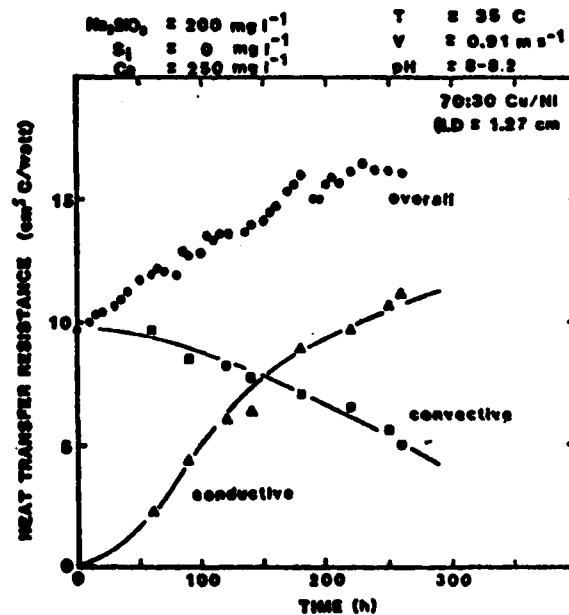


Figure I-10. Relative contribution of convective and conductive resistance to overall HTR due to deposition of calcium carbonate/silicate scale.

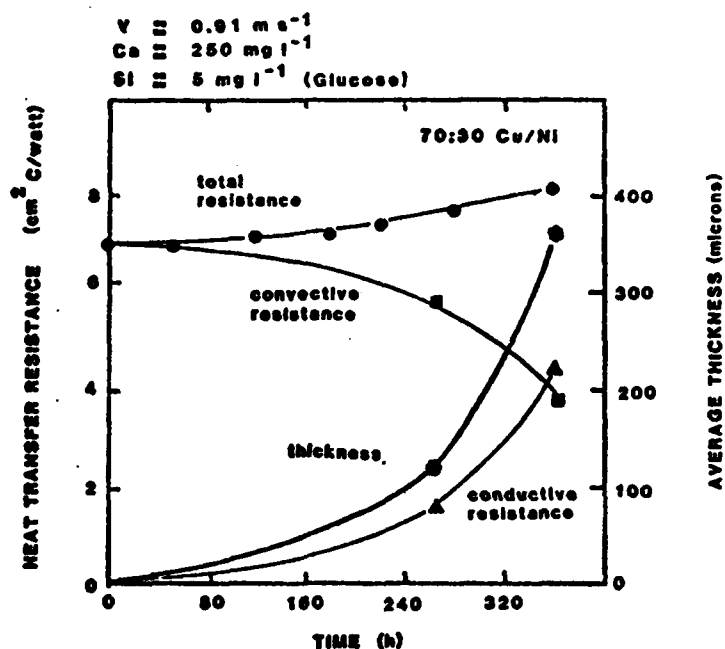


Figure I-11. Relative contribution of convective and conductive resistance to overall (total) HTR due to deposition of combined biofilm/scale.

Field Test

The fouling monitor system has been successfully used [50,57] to monitor fouling in a brackish water cooling system. The goal of one such project [57] was to determine the fouling potential of AL-6X stainless steel heat exchanger tubing. An inside tube wall temperature was chosen for optimum fouling microbe growth as indicated by previous laboratory studies [47]. Results show a rapid build-up of a microbial matrix containing considerable silt debris. Heat transfer fouling appears to plateau at approximately $0.0012 \text{ m}^2 \text{ C/watt}$ ($0.0068 \text{ ft}^2 \text{ }^\circ\text{F hr/Btu}$) within 40 to 60 days regardless of seasonal variation or flow velocity from 0.30 m s^{-1} (1.0 fps) to 0.50 m s^{-1} (1.7 fps).

Test conducted at 0.30 m s^{-1} (1.0 fps). Figure I-12 presents the progression of heat transfer resistance and the fouling factor for the first 100 days of testing at a constant flow velocity of 0.30 m s^{-1} and a constant inside tube wall temperature of 35 C (95°F). In addition to the obvious increase in heat transfer with time, several other features are noteworthy:

1. On day 24 and day 62, momentary flow excursions occurred which increased flow to 0.90 m s^{-1} . These flow excursions were associated with sudden drops in heat transfer resistance as a result of the fouling deposit sloughing off.

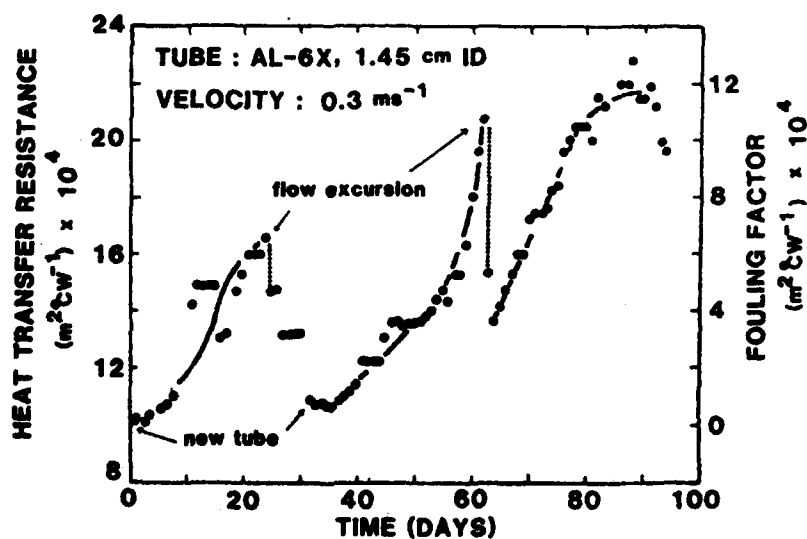


Figure I-12. Progression of HTR at constant flow rate ($0.3 m s^{-1}$) and constant temperature ($35 C$).

- On day 30, the AL-6X was replaced with a new AL-6X tube of identical dimensions (test 2). The fouling factor returned to within 3 percent of its original value. Figure I-13 shows the progression of heat transfer resistance for the first 30 days (test 1) superimposed on test 2 results. Progression of heat transfer resistance was almost identical for both tests despite seasonal variation resulting in change in bulk water temperature from $17 C$ to $27 C$.

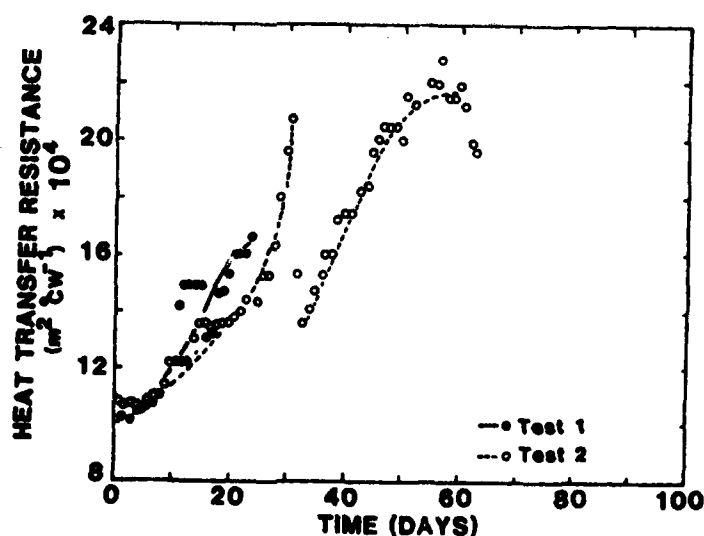


Figure I-13. Progression of HTR for test 1 (Figure I-13) superimposed on test 2 at a constant flow rate ($0.3 m s^{-1}$) and constant surface temperature ($35 C$).

Figure I-14 presents the progression of fluid friction resistance as friction factor for test 1 and test 2 at a low velocity of 0.3 m s^{-1} . A similar progression as heat transfer resistance is observed. Of particular interest, is the drop in the frictional resistance at day 62 corresponding to the drop in heat transfer resistance attributed to the 0.90 m s^{-1} flow excursion.

Test conducted at 0.50 m s^{-1} (1.70 fps). Figure I-15 shows the progression of heat transfer resistance and the fouling factor with time for a flow velocity of 0.50 m s^{-1} and a constant inside wall temperature of 35 C . No flow excursion or other perturbations occurred during the 80 day test period. The progression of fouling followed a typical sigmoidal pattern and plateau which is seen for almost any measurement of fouling progression [48].

The plateau fouling factor was virtually the same as for 0.30 m s^{-1} . Furthermore, the rate of fouling at 0.50 m s^{-1} is very similar to that observed at 0.30 m s^{-1} .

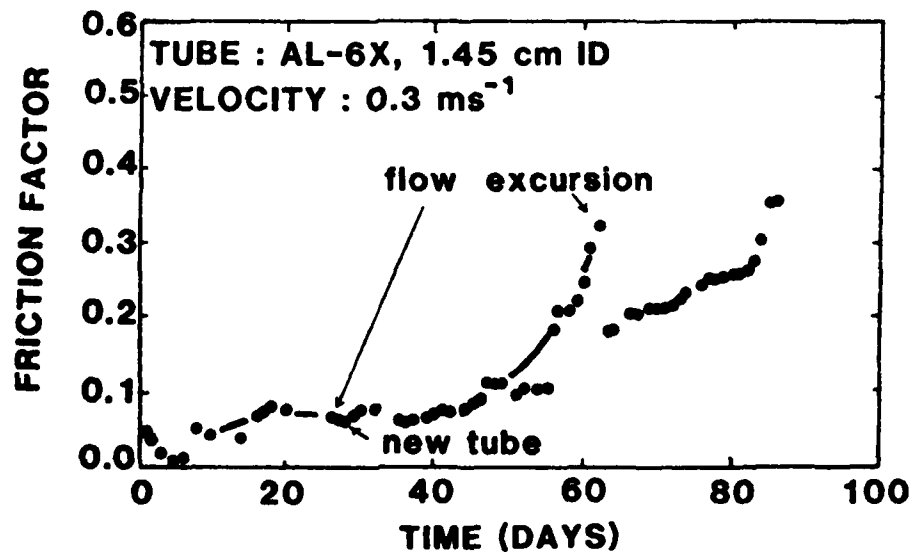


Figure I-14. Progression of friction factor with time at a constant flow rate (0.3 m s⁻¹).

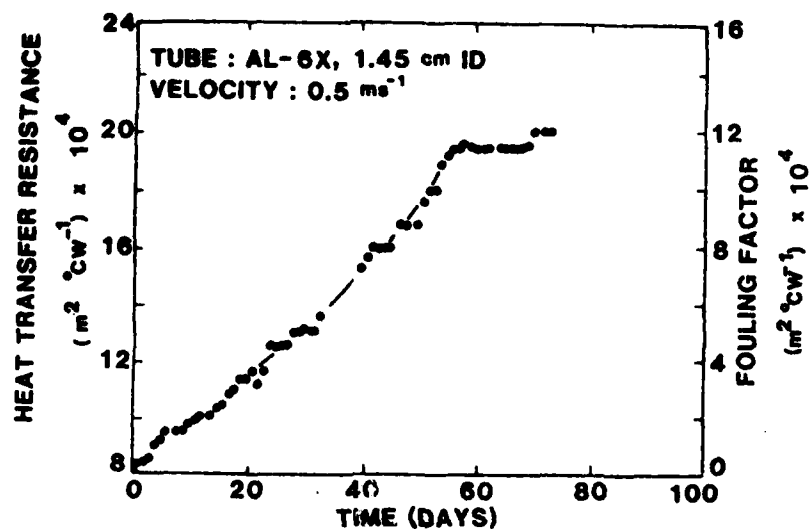


Figure I-15. Progression of HTR at a constant flow rate (0.5 m s⁻¹) and constant surface temperature (35 C).

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NOMENCLATURE

A	= wetted surface area	(L^2)
C_P	= specific heat of the fluid	$(L^2 \tau^{-1} T^{-1})$
f	= friction factor	(dimensionless)
h	= convective heat transfer coefficient	$(M \tau^{-1} T^{-1})$
k	= fluid thermal conductivity	$(ML \tau^{-1} T^{-1})$
k_B	= apparent thermal conductivity of biofilm	$(ML \tau^{-1} T^{-1})$
k_M	= thermal conductivity of the metal block	$(ML \tau^{-1} T^{-1})$
k_D	= thermal conductivity of the deposit	$(ML \tau^{-1} T^{-1})$
k_T	= thermal conductivity of the tube	$(ML \tau^{-1} T^{-1})$
L	= distance between pressure ports	(L)
l	= length of the metal block	(L)
N	= rate of nutrient consumption by biofilm	$(ML^{-2} \tau^{-1})$
q	= heat input to the metal block	$(ML^2 \tau^{-2})$
R_A	= net rate of transport and adsorption of cells, organic and inorganics to the surface	$(ML^{-2} \tau^{-1})$
R_B	= net biofilm accumulation rate	$(M \tau^{-2})$
R_D	= rate of detachment of biofilm	$(ML^{-2} \tau^{-1})$
Re	= Reynolds Number	(dimensionless)
R_f	= fouling factor	$(M^{-1} t^3 T)$
r_i	= radial distance to inner thermistor	(L)
r_{ii}	= radial distance to outer thermistor	(L)
r_1	= inside radius of the tube	(L)
r_2	= outside radius of the tube	(L)
r_I	= radial distance to the deposit ($r_1 - \Delta h$)	(L)

t	= time	(t)
T_{B1}	= inlet bulk water temperature	(T)
T_{B2}	= outlet bulk water temperature	(T)
$T_{B(avg)}$	= average bulk water temperature	(T)
T_i	= temperature at r_i	(T)
T_{ii}	= temperature at r_{ii}	(T)
Th	= thickness of the deposit	(L)
U^{-1}	= overall heat transfer resistance	($M^{-1} t^3 T$)
U_{cond}^{-1}	= convective heat transfer resistance	($M^{-1} t^3 T$)
U_{conv}^{-1}	= convective heat transfer resistance	($M^{-1} t^3 T$)
$U_{overall}^{-1}$	= overall heat transfer resistance	($M^{-1} t^3 T$)
v	= mean fluid velocity	($L t^{-1}$)
Y	= mass of biofilm produced per unit nutrient mass consumed	(dimensionless)
Δp	= pressure drop across length L	($ML^{-1} t^{-2}$)
μ	= fluid viscosity	($ML^{-1} t^{-1}$)
ρ_f	= fluid density	(ML^{-3})
ρ	= biofilm density	(ML^{-3})
δ_1	= viscous sublayer thickness	(L)
e	= effective height of roughness element	(L)

SECTION II. BIOFOULING AND CORROSION

INTRODUCTION

Piping systems and heat transfer surfaces in the marine environment are subject to the effects of organic and inorganic fouling. The detrimental effects of these fouling deposits include increased frictional resistance for fluid flow, increased heat transfer resistance, and, under certain conditions, an accelerating effect on corrosion of some materials.

Frictional resistance increases the power requirements for sea water pumping and reduces delivery capacity of the system. Heat transfer resistance results in a reduction in thermal efficiency of heat transfer equipment and an associated increase in energy costs.

Biofouling

Biological fouling is perhaps the least understood of all fouling processes. When a clean surface is exposed to sea water, rapid adsorption of organic molecules (primarily polysaccharides and glycoproteins) takes place (Corpe, 1973; Loeb and Neihof, 1973; Sechler and Gunderson, 1972; DePalma *et al.*, 1978). This organic adsorption is followed by the accumulation of marine bacteria (Corpe, 1973). The rates of bacterial accumulation vary on different surfaces and in different environments. Sechler and Gunderson (1972) found that bacteria may adsorb to metals at rates proportional to that with which nutrients sorb, a condition predicated by relative galvanic activity. Bryers and Characklis (1981) found, in fresh water, that biofilm accumulation increased linearly with increasing suspended biomass concentration and also increased with increasing suspended organism growth rate.

Extensive laboratory studies of the biofouling process and its effects have been conducted by Characklis and co-workers in fresh water systems (Characklis *et al.*, 1982; Characklis, 1981; Bryers and Characklis, 1981; Picologlou *et al.*, 1980; Characklis, 1980). A proposed model divides the biofouling process into three phases: (1) initial biofilm formation when the microorganisms first begin to colonize; (2) exponential accumulation of biofilm mass associated with an increase in energy losses (heat transfer resistance and frictional resistance); (3) steady-state biofouling when a plateau or asymptote in biofilm accumulation exists.

Biofouling Control Methods

Attempts to control biofouling in marine heat exchangers and piping systems have met with varying degrees of success. Chlorination and, to a lesser extent, other chemical oxidants (ozone, hydrogen peroxide, etc.) have been effectively used to combat biofouling. Copper alloys have been widely used due to their inherent "toxicity" towards many forms of marine life.

The effectiveness of chlorine in treating biofouling, including microbial slime and macrofouling organisms such as molluscs, barnacles, bryozoa, hydroids, sponges, and tunicates, has been well established (Marine Research, 1976; Bongers and O'Conner, 1977).

Chlorine can be added directly to sea water in the gaseous form or generated electrolytically. The result in both cases is the formation of hypochlorous acid which will, depending on pH, further dissociate into hypochlorite. The reaction products of chlorine are consumed in sea water not only by the organisms for which they are intended, but also by reactions with bromide, nitrogen compounds (e.g., ammonia), organic detritus and metal surfaces. All of these factors combined contribute to the chlorine demand of the sea water system and determine the relative effectiveness and cost of chlorination as a means of controlling biofouling.

Numerous researchers have reported that copper containing alloys are toxic to marine organisms (Huguenin and Ansuini, 1980; Ritter and Sutor, 1976; Nosetani *et al.*, 1979). Dexter (1974) conducted microfouling studies in warm tropical waters of the open ocean. He demonstrated that a film 50-125 μm thick could form in less than a month in warm surface waters. A continuous layer of diatoms and bacteria embedded in slime were observed on samples of 90-10 and 70-30 copper-nickel. DePalma *et al.* (1981) investigated biofouling and corrosion on titanium and copper-nickel (70-30) in sea water and observed that attached organisms produced more extracellular proteoglycan material on the titanium surface than on the copper-nickel. Furthermore, corrosion products on the copper-nickel surface were partially embedded in the biofilm and periodic sloughing of the combined biofouling and corrosion product film occurred.

Corrosion

Sea water is a very complex solution of numerous salts and dissolved gases plus suspended silt, living organisms and decaying organic matter. The corrosion of metals in sea water is affected by many factors including oxygen, salinity, pH, temperature, and biological activity.

Some metals, such as titanium, form very thin, tightly adherent protective oxide films in sea water which are essentially inert (Tracor Marine, 1978). Protective corrosion product films on copper and its alloys, by comparison, grow much more slowly and are affected significantly by thermohydrodynamic conditions.

In sea water, the corrosion product on copper-nickel alloys is predominately Cu_2O (cuprous oxide) irrespective of alloy composition (North and Pryor, 1970). Often, the basic chloride atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$), a bulky, green nonprotective corrosion product, forms overlying the Cu_2O layer. A carbonate salt, malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), may form competitively with the basic chloride salt depending upon local surface pH and total inorganic carbon concentration (Bianchi and Longhi, 1973). Temperature, depth, and biological activity are the main factors influencing the total inorganic carbon concentration in sea water.

The Cu_2O corrosion product is the adherent, protective film responsible for the low corrosion rates observed on Cu-Ni alloys in unpolluted, aerated, sea water. According to Efird and Anderson (1975), the corrosion rate of 70-30 CuNi in flowing sea water (0.6 m s^{-1}) was approximately $2.0 \mu\text{m yr}^{-1}$ after 14 years exposure, but had stabilized at that value after 4 years. Efird (1975) further studied the relationship between corrosion product formation and biofouling resistance of copper base alloys. He proposed the following model to describe the process:

1. Initial formation of a protective Cu_2O film.
2. Subsequent hydrolysis of Cu_2O to a loosely adherent $\text{Cu}(\text{OH})_2 \cdot 3\text{CuCl}_2$ film.
3. Fouling attachment to the $\text{Cu}(\text{OH})_2 \cdot 3\text{CuCl}_2$ film.
4. Removal of the fouling organisms with the basic chloride film leaving the Cu_2O intact.

As the Cu_2O corrosion product film grows in sea water, copper ions and electrons must pass through the film to support anodic and cathodic half reactions. It has been shown experimentally (North and Pryor, 1970) that alloying additions of nickel and iron to copper improve corrosion resistance. The mechanism proposed is the incorporation of Ni and Fe ions into the highly defective p-type Cu_2O corrosion product film as "Dopants," thereby altering the defect structure. The result is a protective corrosion product film possessing relatively low electronic and ionic conductivity.

The corrosion of copper-nickel alloys in aerated, unpolluted, sea water is cathodically controlled by oxygen reduction. Dissolved oxygen retards corrosion by the promotion of a protective oxide film on the copper-nickel alloy surface, but increases the rate of corrosion by depolarizing cathodic sites and oxidizing cuprous ions to the more aggressive cupric ions. Other factors, such as velocity, temperature, salinity and depth affect dissolved oxygen transport and content in sea water thereby influencing the corrosion rate.

Soluble complexes of cuprous (CuCl_2^- , CuCl_3^-) and cupric (CuCl^+ , CuCl_2^+ , CuCl_3^+ , $\text{Cu}(\text{CO}_3)_2$, etc.) ions are thermodynamically feasible in seawater. These complexes form at rates dependent upon the available concentration of Cu^+ and Cu^{++} ions. Complexation with organic ligands has been studied (Compton, 1973) and is hypothesized as a mechanism for the increased corrosivity of natural sea water over equivalent saline solutions. Organic complexation may be an important factor associated with biological activity and may be critical in biologically accelerated corrosion.

Polluted sea water has been cited (Gilbert, 1954) as the most important factor contributing to failure of copper alloy marine condenser tubes. The primary cause of accelerated attack of copper base alloys in polluted sea water is due to the presence of sulfide. The principal sources of sulfide in sea water are (1) the action of sulfate reducing bacteria, and (2) the putrefaction of organic sulfur compounds resulting in the formation of organic sulfides which can cause localized corrosion of copper nickel alloys in sea water (Bates and Popplewell, 1974).

Microbiological fouling of copper-nickel alloys in sea water and its influence on the corrosion process is not well-understood in comparison to the electrochemical processes. Corrosion scientists and engineers have studied the effects of organically derived sulfide and sulfur compounds, as previously mentioned, the effect of chlorination on corrosion (LaQue, 1950; Stewart and LaQue, 1952), and mechanical biofouling control methods with and without chlorination (Lewis, 1982). Sophisticated surface analytical techniques such as x-ray photoelectron spectroscopy (XPS) and scanning auger microscopy (SAM) have been utilized to study the development of inorganic and biological fouling layers on copper based alloys (Castle and Epler, 1981).

Most of these studies have been phenomenological, however, and have not adequately modelled the mechanisms of microbial attachment to copper-nickel surfaces and the role of microorganisms in the corrosion process. The following study is intended to identify some of the important aspects of microbial fouling and microbially-assisted corrosion of copper-nickel.

EXPERIMENTAL METHODS

Recycle Tubular Loop (RTL)

Three parallel recycle tubular loops (RTL) of the type shown in Figure II-1 were used in this research. Pertinent dimensions and materials of construction are given in Table II-1. A detailed description of the RTL system, analytical methods, and operation is presented elsewhere (Characklis and Zilver, 1983). Important features of the RTL include:

Each RTL is made predominantly of 0.625 in (0.0159 m) O.D. heat exchanger tubing with a wall thickness of 0.049 in (0.00124 m). Titanium or 70-30 copper-nickel tubing was used depending on the experimental design. A section of tubing is fitted with ports for measuring *pressure drop*. A polyvinyl chloride shell encloses another section of tubing to form a *heat exchanger* which is used to control bulk water temperature by removing excess heat build-up from pumping friction; a thermo-regulator detects when cooling is necessary and opens a solenoid valve to pass cold tap water over the section of tubing. A *test section* comprised of 10 removable sections of tubing each 2 in (0.051 m) long is included for surface analyses of the deposit mass and the fouled surface (Figure II-2).

A *flow meter* which measures cumulative water flow is used with a timer to calculate fluid flow velocity.

Water is recycled through the RTL by a *centrifugal pump* with a chemically resistant, phenolic head. Fluid flow rate is controlled manually by a ball valve located downstream of the flow meter.

A *pH* controller is not included but the buffering capacity of the aquarium salt maintains pH between 8.2 and 8.4.

A *glass mixing tank* is used for housing the thermo-regulator and for feed water input.

Feed Water Composition

Feed water consists of 11,300 mg ℓ^{-1} *aquarium salt* (Instant Ocean) for dilution to which one or more of the following may be added:

Trypticase Soy Broth (TSB) nutrition for microbial growth to give a nutrient loading rate (R_L) of either 0.92 or 9.2 mg $m^{-2} \min^{-1}$.

Bacterial cells from a fixed film chemostat inoculated with *Pseudomonas atlanticus*, *Flavobacterium*, *Vibrio alginolyticus*, *Pseudomonas alcaligenes* and *Desulfovibrio*. The chemostat is continuously fed with 100 mg ℓ^{-1} Trypticase Soy Broth in 11,300 mg ℓ^{-1} salt water (Instant Ocean). Continuous analysis of chemostat output for a 7 month period shows $4.77 \times 10^9 \pm 8.20 \times 10^9$ total cells per hour and $3.37 \times 10^9 \pm 9.05 \times 10^9$ viable cells per hour.

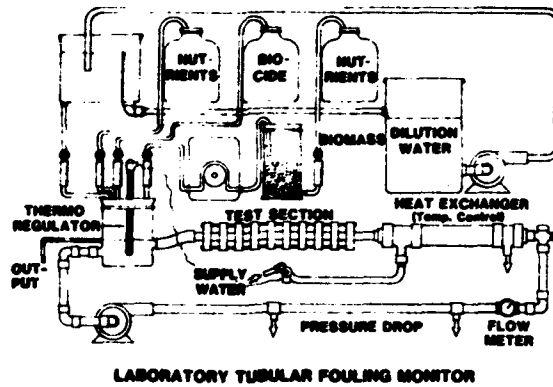


Figure II-1. Schematic of recycle tubular loop.



Figure II-2. Recycle tubular loop test section.

Table II-1. Pertinent Dimensions and Construction Materials of the Recycle Tubular Loop

Liquid Volumes		V (m³)	
Tubing (CuNi or Ti, PVC and Tygon)		0.00095	
Centrifugal Pump (phenolic)		0.00018	
Flow Meter (PVC)		0.00024	
Mixing Tank (glass)		0.00035	
Total Volume		0.00172	
Tubing Lengths and Inside Diameters		L (m)	ID (m)
Heat Exchanger (CuNi or Ti)		0.76	0.0134
Pressure Drop Section (CuNi or Ti)		1.22	0.0134
Test Section (CuNi or Ti): 10 0.051 μ m long sample tubes)		0.51	0.0134
Connecting Tubing (CuNi or Ti)		1.21	0.0134
Total Length of Metal Tubing		3.70	
Connecting Tubing (Tygon)		0.16	0.0159
Connecting Tubing (PVC)		1.30	0.0175
Total Length		5.16	
Surface Area		m²	
Total Area		0.1033	

Chlorine at a loading rate of $0.92 \text{ mg m}^{-2} \text{ min}^{-1}$ either continuously or periodically (one hour every 24 hours).

Filtration of the influent aquarium salt is used to minimize microorganisms in some experiments.

Analytical Methods

Analytical methods are described in detail elsewhere (Characklis and Zilver, 1983; Characklis *et al.*, 1982). Important features of these methods include:

Sampling for bulk water analysis is directly from the mixing tank using a sterile pipet. Surface samples are taken from the removable sample tubes by scraping the sample from the surface with a sterile rubber policeman into a beaker of sterile distilled water. All samples are homogenized with a high speed, sharp-bladed, mixer.

Total cell counts are measured by the AODC epifluorescence technique (Zimmerman and Meyer-Riel, 1974).

Viable cell counts are by the spread plate technique (APHA, 1976).

Deposit mass is measured by drying the removable sample tube for three hours at 100°C and then weighing the tube. The tube is then cleaned (deposit mass removed), dried and weighed again. The deposit mass is the difference between the dry fouled sample tube mass and the clean tube mass.

Corrosion rates are measured from the difference between mass of the sample tube at the experiment start and the cleaned sample tube at the experiment end. The difference in mass is divided by the exposure time to determine a rate which is then converted to units of microns per day.

Percent volatile deposit mass is determined on deposit mass scraped from the inside tube surface. Volatile mass is the mass removed by ignition at 600°C for one hour as described in Standard Methods (APHA, 1976).

Chemical analysis of the deposit mass was performed by atomic absorption.

Scanning Auger Microprobe (SAM) measurements were performed using the Phi 595 Model (Physical Electronics).

Chlorine was measured by the amperometric method.

RTL Operation

Table II-2 presents a summary of conditions which were the same for all experiments. Conditions which varied include *tube alloy* (70-30 copper-nickel or titanium), *substrate loading rate* (0.92 or 9.2 mg TSB m⁻² min⁻¹), and *treatment* (chlorination, filtration, or none).

Table II-2. Summary of Conditions which were Identical for All Experiments

Volumetric Feed Rate	1.9×10^{-5} (m ³ min ⁻¹)
Hydraulic Retention Time	90 (min)
Water Temperature	30 (°C)
pH	8.2 - 8.4
Fluid Flow Velocity	54 (m min ⁻¹)
Fluid Shear Stress	3.0 (N m ⁻²)
Salt Concentration	11,300 (mg l ⁻¹)

RESULTS

Control Experiments

Experiments where no biocide has been added are referred to as control experiments. Controls have been conducted to observe the natural progression of fouling on the condenser tube surface. Figure II-3 shows the progression of fouling for the titanium control experiments as indicated by change in Fouling Deposit Mass (M_D). Change in M_D for substrate loadings

(R_L) of both 0.92 and $9.2 \text{ mg TSB m}^{-2} \text{ min}^{-1}$ are indicated. Note, the rate increase in M_D at $R_L = 9.2 \text{ mg m}^{-2} \text{ min}^{-1}$ is approximately three times the fouling rate increase at $R_L = 0.92 \text{ mg m}^{-2} \text{ min}^{-1}$. The progression of M_D is indicated as linear since data are presently not available to justify a more sophisticated analysis. Presumably, as suggested by other work (Characklis, 1980), M_D reaches a plateau level at some point in time. However, for the initial stages of fouling, and for comparison, the linear regression analysis is sufficient.

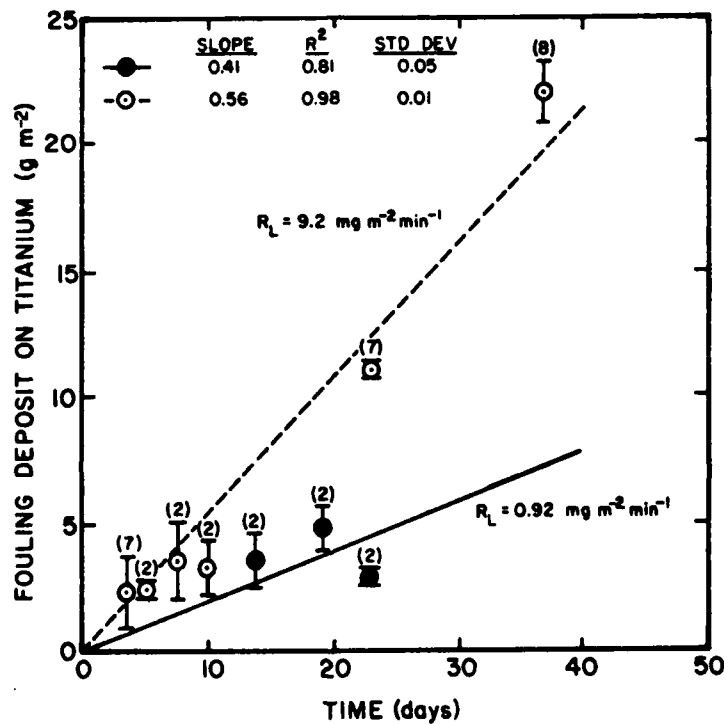


Figure II-3. Progression of fouling deposit mass with time on copper-nickel (regression fit forced through zero).

Figure II-4 shows the progression of M_D with time on copper-nickel tubing for the two substrate loadings. In this case, there is no significant difference between the substrate loadings.

Figure II-5 shows the progression of fouling on copper-nickel and titanium tubing as indicated by change in Volatile Deposit Mass (M_{VD}). The rate increases in M_{VD} are calculated by multiplying the rate increases in M_D by the average percent volatile mass. At $R_L = 0.92 \text{ mg m}^{-2} \text{ min}^{-1}$, the rate increases in M_{VD} for copper-nickel and titanium show no significant difference. However, at $R_L = 9.2 \text{ mg m}^{-2} \text{ min}^{-1}$, M_{VD} accumulates approximately four times faster on the titanium surface compared to the copper-nickel surface.

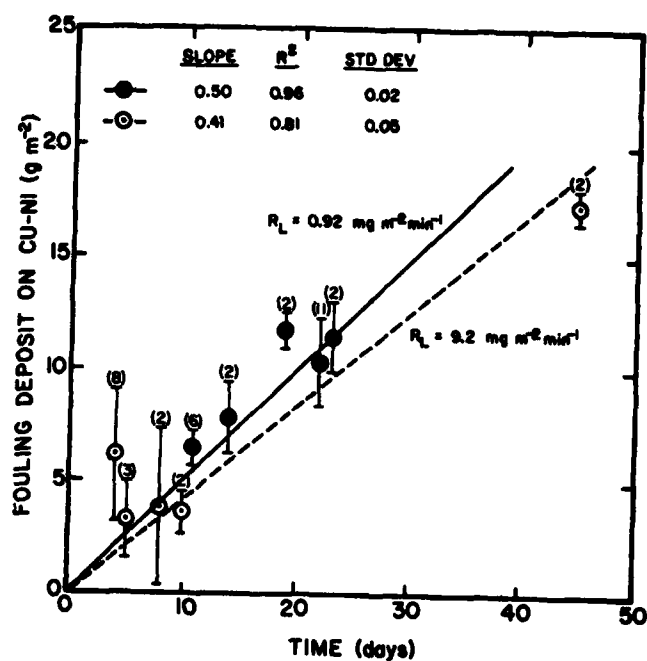


Figure II-4. Progression of fouling deposit mass with time on copper-nickel (slope regression fit forced through zero).

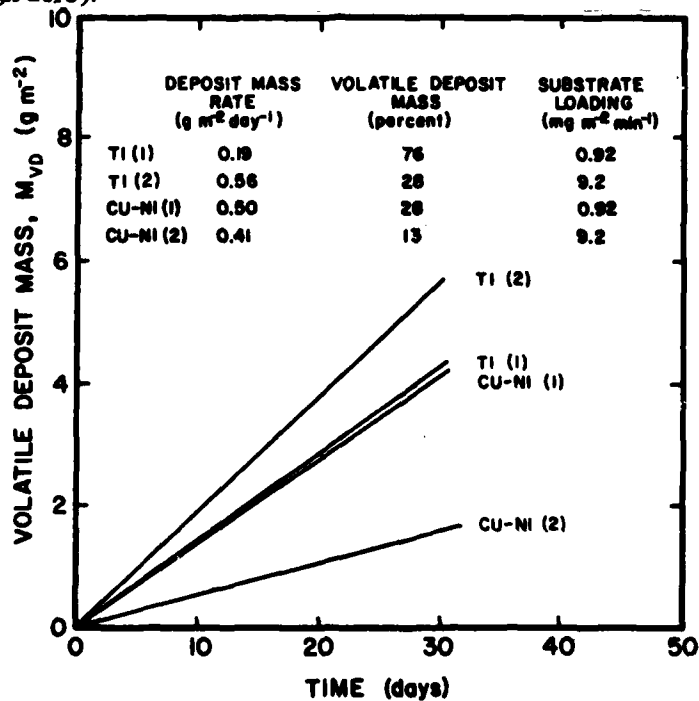


Figure II-5. Progression of volatile fouling deposit mass with time on copper-nickel and titanium.

Measurements of Corrosion Loss (C_L) for all control experiments are summarized in Table II-3. C_L is zero on the titanium tubing and averages 33 microns per year for copper-nickel at $R_L = 0.92 \text{ mg m}^{-2} \text{ min}^{-1}$. Average C_L at the higher substrate loading ($R_L = 9.2 \text{ mg m}^{-2} \text{ min}^{-1}$) is approximately half that at the lower substrate loading.

Table II-3. Corrosion Loss and Volatile Deposit Mass for All Control Copper-Nickel and Titanium Experiments

Alloy	Substrate Loading ($\text{mg m}^{-2} \text{ min}^{-1}$)	Corrosion* Loss ($\mu\text{m yr}^{-1}$)	Volatile* Deposit Mass (percent)
CuNi	0.92	$33 \pm 6(14)$	$28 \pm 9(5)$
Ti	0.92	$0 \pm 0(2)$	$76 \pm 9(2)$
CuNi	9.2	$16 \pm 9(4)$	13(1)
Ti	9.2	—	$28 \pm 11(2)$

*Values given are mean \pm one standard deviation with the # of samples given in parentheses.

Microbial Cell Counts

Total microbial cell counts on the copper-nickel and titanium surfaces, for all control experiments combined, show no significant difference between the two alloys (Figure II-6).

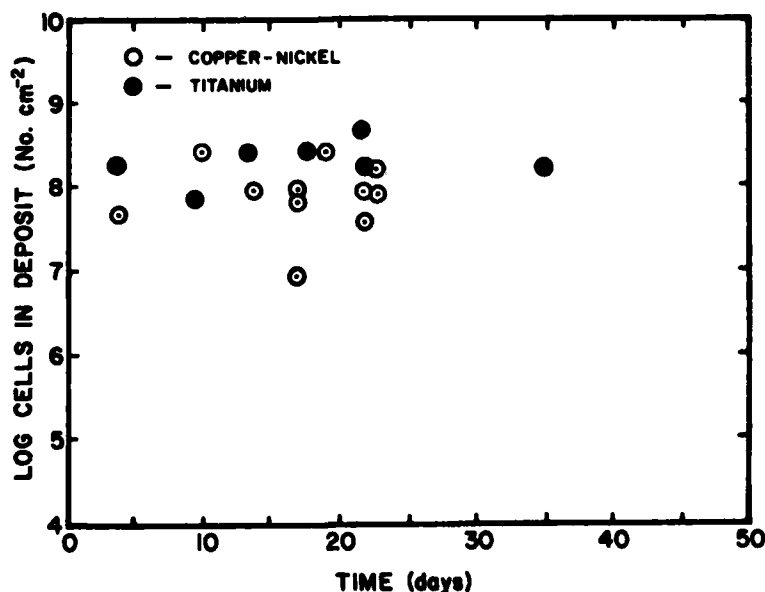


Figure II-6. Total microbial cells within deposit for all control copper-nickel and titanium experiments.

Table II-4 summarizes all total and viable microbial cell counts taken for control copper-nickel and titanium experiments. No significant difference in cell counts between the two alloys is observed for measurements taken from either the tube surface or the bulk water.

Table II-4. Viable and Total Cell Counts in the Bulk Water and in the Deposit Mass for All Control Copper-Nickel and Titanium Experiments

Sample (alloy)	Bulk Water Cells (10^8 cells hr^{-1}) [†]		Attached Cells (10^8 cells cm^{-2})	
	STP*	EPI**	STP*	EPI**
CuNi	$2.0 \pm 2.2(26)$	$4.4 \pm 4.3(28)$	$0.4 \pm 0.32(5)$	$1.1 \pm 0.8(13)$
Ti	$1.6 \pm 1.6(12)$	$4.0 \pm 6.1(16)$	$3.9 \pm 6.9(4)$	$2.2 \pm 1.2(7)$

Note. Values given are the mean \pm one standard deviation with the number of samples given in parentheses.

*STP: standard plate count (viable cells)

**EPI: AODC by epifluorescence (total cells)

[†]Number of cells exiting the reactor per hour in the bulk water flow

Scanning Auger Microprobe Measurements

Scanning Auger Microprobe (SAM) measurements on sample tubes removed at the end of each experiment are summarized in Table II-5. The values are weight percent of each element for the overall surface analyzed. Figure II-7 shows the relationship between weight percent oxygen and the amount of volatile mass removed from the sample tube before the SAM measurement. Note, more oxygen is found on the metal surfaces containing greater attached volatile mass.

Table II-5. Scanning Auger Microprobe Analyses of Elements on Copper-Nickel Surface After Removal of Fouling Deposit Mass

	Cu	Ni	Fe	Mn	O	N	Ca	C	Cl	S
Control	49.7	34.4	2.4	0.7	8.4	0.3	0.4	1.1	2.4	0.6
Filtered	43.8	34.5	0.8	1.8	10.7	0.4	0.5	2.8	3.3	0.3
Chlorinated	75.0	12.3	2.1	1.1	5.2	0.2	0.6	1.4	1.1	0.3
New CuNi	67.6	26.5	1.2	1.6	0.9	0.4	0.6	1.0	2.7	0.5

Chemical Analysis of Deposit Mass

An analysis of elements found within the deposit is presented in Table II-6. Weight, percent of iron, and copper are measured on control copper-nickel sample and a control titanium sample. In addition, a sample of tygon tubing which connects copper-nickel tubing of the RTL to the glass tank, is analyzed to determine if any material from the copper-nickel is

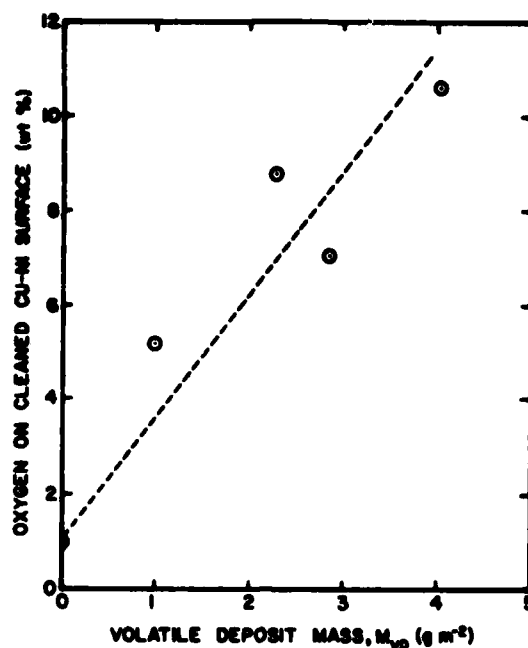


Figure II-7. Weight percent oxygen on copper-nickel versus fouling deposit removed.

deposited elsewhere in the system. Results show considerably more copper in the deposit from the copper-nickel tube compared to the titanium (59 percent for CuNi versus 1.6 percent for the Ti). Weight percent iron changed little. A considerable amount of copper is found on the tygon section. Visual observation indicated a green tint to all deposits found in the RTL with copper-nickel tubing.

Table II-6. Atomic Absorption Analyses of Iron and Copper Within the Fouling Deposit Mass

Sample	Exposure Time (days)	Condition	Percent of Total Deposit Mass	
			Iron	Copper
CuNi	22	Control	1.21	59.12
Tygon	22	Control	0.40	31.80
Ti	23	Control	3.88	1.58

Filtration of Influent Water

In these experiments, the influent water is filtered and no substrate or bacteria is fed to the RTL. These experiments are designed to compare corrosion and fouling with and without bacteria. Contamination of the RTL occurred regardless of efforts to maintain aseptic conditions. However, the organism levels remain approximately an order of magnitude less on the "filtered" RTL surface compared to the control RTL (Table II-7). Note, no difference in corrosion rate of the copper-nickel is observed between the filtered and control experiments.

Chlorination of Influent Water

Chlorine was added to the influent water at a loading rate of $9.2 \text{ mg m}^{-2} \text{ min}^{-1}$ both continuously and periodically for an hour every 24 hours. Figure II-8 indicates the chlorine demand of the copper-nickel tubing. This experiment was conducted as a batch test to observe the reaction of chlorine with copper-nickel tubing. Free chlorine (20 mg l^{-1}) was added to one liter of stirred solution. The amount of copper-nickel tubing added resulted in the same surface area to volume ratio as in the RTL. Chlorine in the distilled water drops to approximately 13 mg l^{-1} in the first 100 minutes and then remains constant. The chlorine exposed to the copper-nickel drops rapidly and, at 300 minutes, is no longer measurable. Combined chlorine in both solutions was always zero.

Table II-8 compares results of the chlorine experiments to corresponding control experiments. The periodic chlorination of titanium is ineffective in reducing accumulation of deposit mass. However, continuous chlorination of titanium reduces M_D at 37 days from 22 g m^{-2} to 4.5 g m^{-2} . Surface cell numbers are reduced on the titanium surfaces exposed to both continuous and periodic chlorination. No significant difference in cell numbers is observed in the bulk water organisms. Only continuous chlorination is applied on the copper-nickel RTL. The results show no significant difference in deposit mass, corrosion rate, or in surface and bulk water organisms.

DISCUSSION

The results of this study do not justify the development of a new theory for microbially-mediated corrosion in Cu-Ni alloys. However, the results are useful for proposing a model to describe the process which may serve as a hypothesis for further experimentation.

A Conceptual Model for Microbially-Mediated Corrosion of Cu-Ni Alloys

The processes of major concern in this experimental system are corrosion of the metal surface and accumulation of fouling biofilm deposit. The processes occur simultaneously and interact with each other. Figure II-9 is a schematic representation of the individual processes contributing to the corrosion and fouling processes. Table II-9 identifies each of the processes designated by a number in Figure II-9.

Table II-7. Fouling Deposit Mass, Corrosion Loss, Percent Volatile, Deposit Mass and Microbial Analysis of Deposit for Control and Filtered Experiments

Sample (alloy)	Exposure Time (days)	Condition	Deposit Mass (g m^{-2})	Corrosion Loss ($\mu\text{m yr}^{-1}$)	Volatile Deposit (%)	Cells in Deposit		
						STP*	(10^7 cells cm^{-2})	EPI** (10^7 cells cm^{-2})
CuNi	45	filtered	$7.5 \pm 4.2(33)$	$14 \pm 11(4)$	53	1.3(1)	0.32 \pm 0.02(5)	
CuNi	45	control	$12.4 \pm 6.1(3)$	$16 \pm 9(4)$	13	8.0(1)	8.6 \pm 1.6(5)	
Ti	37	filtered	$2.0 \pm 3(8)$	--	--	9.3(1)	2.5 \pm 7.0(5)	
Ti	37	control	$22.1 \pm 1.2(8)$	--	36	--	1.5 \pm 5.0(5)	

Note. Values given are the mean \pm one standard deviation with the number of samples given in parentheses.

*STP: standard plate count (viable cells)

**EPI: AODC by epifluorescence (total cells)

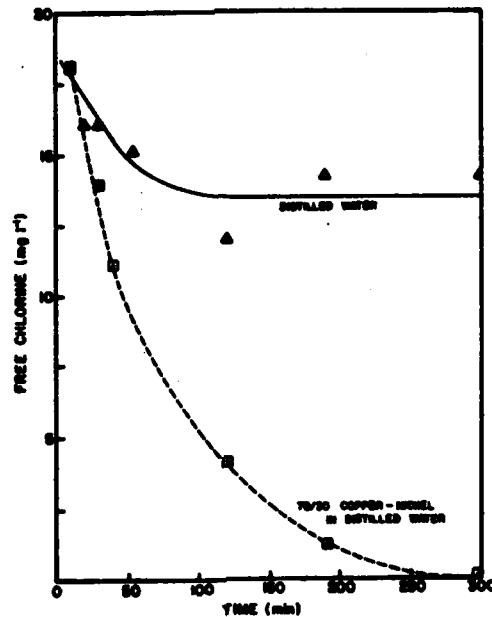


Figure 11-8. Free chlorine versus time for one liter distilled water with and without submerged copper-nickel samples.

Initially, the metal surface is exposed to water containing substrate (an energy source for microbial growth), biomass (microbial cells), and dissolved oxygen. The corrosion process begins with the transport and reaction of oxygen at the metal surface (Process #1) which forms a protective oxide layer of insoluble corrosion products on the metal surface (Process #2). The events leading to corrosion of Cu-Ni alloys and the resulting composition of the surface oxide layer is complex and has been mentioned briefly in an earlier section. Random detachment and attachment of the insoluble corrosion products from the metal surface may occur due to the fluid motion and resulting shear stress (Processes #4 and #5). The detachment of insoluble corrosion products may initiate pit growth in the metal surface due to electrochemical corrosion (Process #3). Soluble corrosion products also diffuse into the bulk fluid (Process #13). The microbial cells (biomass) entering the system are suspended in the bulk fluid and consume substrate (Process #8) and dissolved oxygen (Process #9) resulting in cellular growth and reproduction. Some fraction of the suspended microorganisms attach to the metal surface (Process #11) and continue to consume substrate (Process #7) and dissolved oxygen (Process #10) resulting in growth and reproduction within the fouling deposit. The attached cells also produce extracellular polymers which further enhance attachment and adsorption of more cells, corrosion products, and other debris. The combined cellular and extracellular mass is termed the *biofilm*. A portion of the detached insoluble corrosion products become entrapped in the biofilm (Process #6). The biofilm continues to increase in density and thickness until fluid shear stress causes partial detachment (Process #12). Insoluble corrosion products may also detach with the biofilm (Process #12) thus leaving the

Table II-8. Fouling Deposit Mass, Corrosion Loss, Percent Volatile Deposit Mass and Microbial Analyses for Control and Chlorine Experiments

Sample (alloy)	Exposure Time (days)	Condition	Deposit Mass (g m ⁻²)	Volatile Deposit Mass (%)	Corrosion Loss (μm yr ⁻¹)	Deposit Cells (10 ⁶ cells cm ⁻²)		Bulk Water Cells (10 ⁶ cells cm ⁻³)	
						STP*	EPI**	STP*	EPI**
Ti	10	control	3.3±1.4(2)	--	--	6.1±5.4(2)	118±59(2)	6.3 ±2.3(2)	30 ±17(2)
Ti	10	5 mg l ⁻¹ cl ₂ (periodic for 1 hr each 24 hr)	5.0±0.5(2)	--	--	62 ±75(2)	168±185(2)	8.4 ±.8(2)	39 ±6.3(2)
CuNi	45	5 mg l ⁻¹ cl ₂ (continuous)	10.0±6.4(3)	10(1)	13±10(4)	85(1)	17(1)	0.96±.61(5)	3.2±1.3(10)
CuNi	45	control	12.4±6.1(3)	13(1)	16±9(4)	80(1)	86(1)	2.7 ±2.0(5)	6.3±4.3(10)
Ti	37	5 mg l ⁻¹ cl ₂ (continuous)	4.5±1.3(8)	--	--	0.10(1)	6.2(1)	0.37±.39(4)	4.0±3.2(7)
Ti	37	control	22.1±1.2(8)	--	--	--	150(1)	0.90±0.50(4)	3.6±1.5(7)

Note. Values given are the mean ± one standard deviation with the number of samples given in parentheses.

*STP: standard plate count (viable cells)

**EPI: AODC by epifluorescence (total cells)

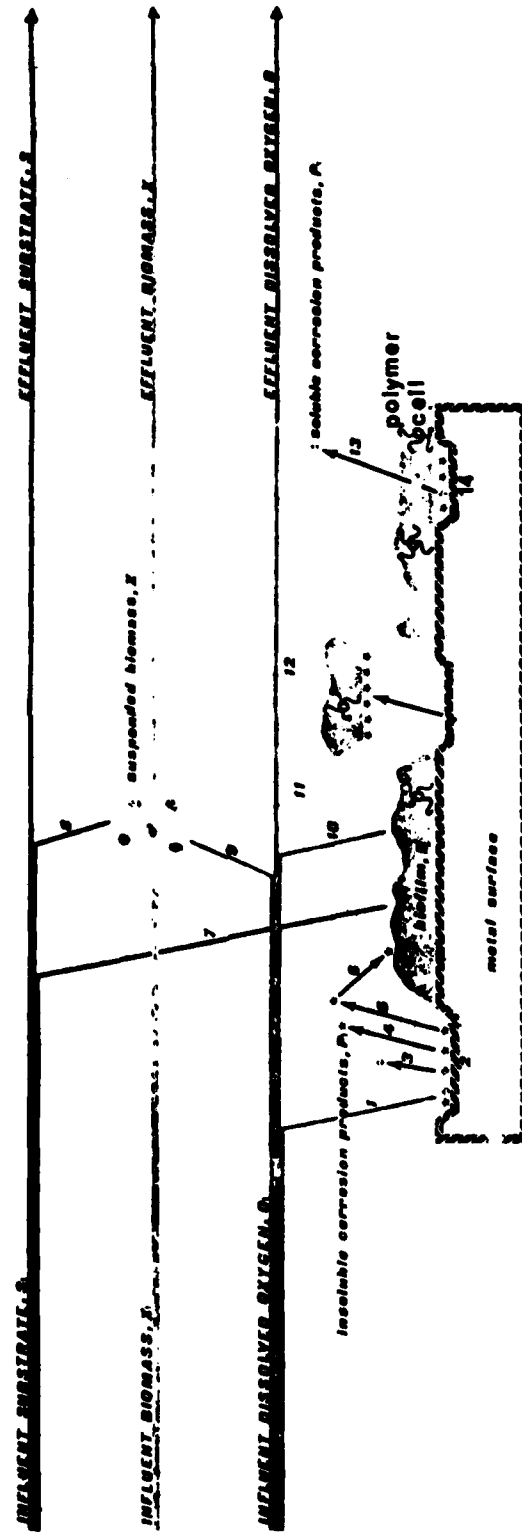


Figure II-9. Schematic representation of individual process contributing to the corrosion and fouling processes.

Table II-9. Explanation of Process Terms Used in Corrosion Model

-
- 1) Dissolved oxygen removal by metal surface
 - 2) Corrosion product formation
 - 3) Soluble corrosion product detachment from metal surface
 - 4) Insoluble corrosion product detachment from metal surface
 - 5) Insoluble corrosion product attachment to metal surface
 - 6) Insoluble corrosion product attachment to biofilm
 - 7) Substrate removal by biofilm
 - 8) Substrate removal by suspended biomass
 - 9) Dissolved oxygen removal by suspended biomass
 - 10) Dissolved oxygen removal by biofilm
 - 11) Suspended biomass attachment to biofilm
 - 12) Biofilm and insoluble corrosion product detachment from metal surface
 - 13) Soluble corrosion product diffusion through biofilm
 - 14) Anaerobic corrosion product formation
-

metal surface more susceptible to corrosion processes. Soluble corrosion products are able to diffuse directly out of the biofilm and enter the bulk fluid. After the biofilm has reached a certain thickness, anaerobic conditions form in the lower layers. These conditions are favorable for proliferation of sulfate-reducers which form sulfide and may lead to accelerated corrosion (Process #14).

A mathematical model has been developed to simulate this system and is presently being tested. The equations are an approximation of the processes occurring in the system. The initial calculations can serve to identify the dominant processes or rate-controlling processes. The results can be used to formulate hypotheses for experimental testing and for experimental design.

Influence of Substrate Loading Rate on Deposition

The accumulation of fouling deposit on a condenser tube surface is the net result of production and depletion processes. Prominent among the production processes are microbial metabolic processes and adsorption. Detachment or sloughing of deposit is perhaps the most important depletion process. Detachment may be quite important in explaining behavior in Cu-Ni alloys which are continuously releasing corrosion products into the bulk water.

An increase in substrate loading rate, R_L , significantly increased the amount of deposit accumulating on the titanium alloy as indicated in Figure II-3. The volatile fraction of the deposit (organic component, including microbial cells, plus carbonates), however, decreased with increasing R_L (Table II-3). The results suggest that at higher loading rates, dissolved oxygen was depleted in the lower layers of the biofilm and anaerobic microenvironments existed. Anaerobic metabolism generally results in a lower volatile solids content.

R_L had no effect on total deposit accumulation on the Cu-Ni alloy (Figure II-4). The volatile content of the deposit in the Cu-Ni was higher at the lower R_L as observed in the Ti alloy. The volatile deposit mass was significantly lower in the Cu-Ni as compared to the Ti tube at the high substrate loading (Figure II-5). At low substrate loading, volatile deposit mass was essentially the same in both alloys. The relative ratio of volatile-to-total solids in the two alloys is predominantly influenced by the corrosion products observed in the Cu-Ni fouling deposits. The lower volatile deposit mass on the Cu-Ni is not easy to rationalize. One possibility is that the microorganisms' metabolism is altered by the Cu or Ni in the deposit, e.g., the organisms' extracellular polymer substance (EPS) production may be influenced by the presence of Cu.

The total and viable number of microbial cells in the deposit varied little between experiments or between alloys (Figure II-6). These preliminary results suggest that Cu-Ni alloys are not very "toxic" to microorganisms (in contrast to macroorganisms). On the other hand, Cu-Ni may influence certain microbiological metabolic functions.

The results can be summarized as follows:

- Deposit mass increases with increasing R_L in the Ti alloy because more nutrients are available for microbial metabolism (Figure II-3).
- Deposit mass in the Cu-Ni alloy does not increase with R_L (Figure II-4) because much of the deposit consists of corrosion products as evidenced by the low deposit volatile fraction as compared to the Ti alloy.
- The change in deposit volatile fraction with different substrate loading rates may be due to increases in extracellular polymer substances (EPS) since cell numbers did not change.
- At higher R_L , dissolved oxygen may not penetrate the entire depth of the biofilm resulting in anaerobic microbial activity in the lower layers. Anaerobic biofilms generally exhibit lower volatile solids content (Metcalf and Eddy, 1972).

The hypothesis regarding oxygen is apparently contradicted by results of the Scanning Auger Microprobe (Table II-5) which indicated elevated oxygen contents on the metal surface with increasing deposit mass (Figure II-7). However, the oxide layer on the alloy most probably forms early in the experiment prior to biofilm formation. Consequently, the oxide layer may determine the amount of biofilm deposit which forms (Figure II-7). Metal oxides vary in the degree to which they affect microbial processes and may not be nearly as active as the pure metal. Therefore, the oxidized Cu-Ni surface, although not "toxic," may provide an "inhospitable" surface for the microorganisms.

Increased R_L resulted in decreased corrosion rates in the Cu-Ni alloy (Table II-3). However, the influence of R_L on corrosion is most probably an indirect effect. The influence of the deposit mass and its constituents (volatile mass and microorganisms) on corrosion, however, is probably more consequential and is discussed below.

Influence of Deposit Mass on Corrosion Rate of Cu-Ni

Increasing R_L has no effect on deposit mass in the Cu-Ni alloy but decreases the volatile content of the deposit. This is related to the fact that more corrosion occurs at low loading rates (Table II-3) and a significant portion of the deposit consists of corrosion products (Table II-6). Since total and viable cell numbers are relatively constant, several alternative hypotheses are advanced to explain the increased corrosion rate at low R_L :

- At low R_L , microbial cells produce more EPS (Trulear, 1982) and, thereby, increase the deposit volatile content although the deposit cell numbers remain relatively constant. The EPS, composed essentially of polyelectrolytes, acts as an electron source or sink to perpetuate or accelerate corrosion.
- At higher R_L , a significantly lower dissolved oxygen flux reaches the Cu-Ni surface (as a result of microbial activity) thus reducing corrosion rate.
- At higher R_L , metabolism of the deposit microorganisms changes in some other unknown manner resulting in decreased corrosion rate.

More experiments are necessary to reproduce and convincingly explain the increased corrosion rate of Cu-Ni at lower substrate loading rate. The precision and accuracy of total and viable cell enumeration must be improved to quantitatively prove any mechanism. Experiments with monocultures or defined microbial communities may be necessary to improve such measurements.

Influence of Microbial Cell Numbers on Corrosion Rate of Cu-Ni

The experiment conducted with filtered sea water may help reduce the choices among hypotheses. The filtered sea water contained no microorganisms nor any trypticase soy broth (TSB) as a microbial energy source. Thus, any organisms in the system were contaminants and grew on chemical contaminants in the artificial seawater or dilution water. The result was a deposit with dramatically lower viable cell counts and significantly lower total cell counts (Table II-7). Despite the reduced number of microorganisms in the deposit, no difference in corrosion rate was observed. Several explanations for these observations are possible including the following:

- The number of microorganisms in the deposit does not influence corrosion rate.
- The dissolved oxygen concentration in the filtered experiment was much higher and increased corrosion rate enough to cancel any effect due to decreased level of microbial activity.
- The deposit organisms in the filtered experiment were significantly different from those in other experiments.
- The absence of organic substrate increased corrosion rate in the filtered experiment as much as microorganisms increased corrosion rate in the control experiments.

Detachment of the Fouling Deposit and Corrosion Rate in Cu-Ni

The model for microbially-mediated corrosion described above includes a term for detachment of fouling biofilm deposit from the tube surface. This process may influence corrosion rate substantially. When a portion (or a "patch") of deposit detaches, the metal surface left exposed will be subject to a considerably different microenvironment from the bare metal (i.e., metal surface with little or no deposit). As a consequence, a differential electrolytic cell may form increasing the potential for localized corrosion.

Chlorine Treatment and Corrosion of Cu-Ni Alloys

Chlorine is a very reactive compound and, hence, an effective bactericide. Chlorine is a strong oxidant which oxidizes many organic compounds and is known to depolymerize polymers of microbial origin (Characklis and Dydek, 1976). Therefore, chlorine has been used as an anti-microbial fouling treatment for many years. Recently, environmental concerns have encouraged searches for new, effective, yet environmentally safe, treatments. Nevertheless, chlorine is still widely used as a cooling water treatment.

Because of its reactive nature, chlorine treatment is frequently ineffective because it is consumed in undesirable side reactions, i.e., "chlorine demand" reactions. Usually, the chlorine demand is due to reduced inorganic compounds or organic compounds in the cooling water. However, Cu-Ni alloys also present a chlorine demand.

This study was conducted in artificial sea water. When chlorine is added to sea water containing bromide ion, the bromide is rapidly oxidized to bromine and the chlorine reduced to chloride. The chemistry of the reaction has been described elsewhere. As a result, and because no distinction was made between chlorine and bromine in our measurements, the combined chlorine and bromine will be referred to as "halogen" below.

Halogen demand. Figure II-8 presents data from a halogen demand experiment. The results clearly indicate a high halogen demand for the Cu-Ni tube section. A halogen residual was never observed in the chlorination experiments as a result of the halogen demand presented by the metal tube, the sea water, and the trypticase soy broth.

Influence of halogen on deposit mass. Halogen treatment, in general, reduced deposit accumulation. The more dramatic effect was observed in the Ti tubes. Halogen treatment had little effect on deposit mass in the Cu-Ni tube nor did it influence microbial cell counts in the deposit or in the bulk water. The high halogen demand of the Cu-Ni tube surface area, TSB, and the artificial sea water resulted in no measurable halogen residual and, hence, partially explains the negligible effect of halogen on the accumulation of fouling deposit.

In the Ti tubes, the influence of halogen on total deposit mass was much more dramatic for at least two reasons:

1. The deposit mass in the Ti tubes contained significantly greater amounts of volatile components, i.e., microbial mass.
2. The Ti tube had little, if any, halogen demand.

Total and viable cell numbers in the deposit as well as in the bulk water were reduced significantly in the Ti system as a result of halogen treatment. The lack of halogen demand at the tube surface may influence the bactericidal nature of the halogen as compared to its effect in the Cu-Ni system. However, the influence of the Cu-Ni corrosion products trapped in the deposit may have also influenced the reactivity of the halogen.

Influence of halogen treatment on corrosion rate in Cu-Ni. Table II-8 indicates no significant effect of halogen treatment on corrosion rate of Cu-Ni. If halogen had significant contact with the Cu-Ni surface, considerable corrosion would be expected due to its high halogen demand. Since no significant corrosion was observed, chlorine may have been consumed in undesirable side reactions and may not have been penetrating the fouling deposit to the Cu-Ni surface. Additionally, Cu-Ni may serve as a catalyst for halogen reduction and, if so, little corrosion would occur as a result of a halogen reduction. More experiments are necessary to determine if a higher halogen loading rate would reduce fouling but, at the same time, increase corrosion rate.

Limitations of the Study

This study was conducted in the laboratory in order to control environmental conditions and to isolate the various processes which influence fouling and corrosion. Consequently, there are several factors which must be considered in interpreting these data or extrapolating the results for field applications. The following limitations were apparent during the investigation and serve as starting points for further experimentation:

- The microbial population was an undefined mixed culture. Changes in dominant species undoubtedly occurred between experiments in which environmental variables were adjusted. The specific influence of a specific organism on fouling and corrosion is unknown except for some few instances.
- The corrosion loss measurements and SAM results quoted represent values over the tube surface. The average values are not a true representation of the corrosion process and, generally, underestimate the potential damage from pitting or crevice corrosion. Pits were observed and were analyzed in more detail elsewhere (Characklis and Zilver, 1983).
- Artificial sea water was used. The problems associated with its use, if any, are not clearly documented.
- The substrate used for microbial growth, TSB, is not representative of all waters. Nevertheless, TSB is a diverse mixture of organic compounds, many of which are found in natural environments. The concentrations used are representative of natural waters.

- The time of exposure for the Cu-Ni tubes was short compared to its projected lifetime in a condenser or other applications. The ultimate effect of fouling and corrosion over a long period due to our experimental manipulations is unknown.
- Sampling of the deposit mass required procedures which may have disturbed or influenced the total amount of oxide layer or other corrosion products residing on the tube surface after deposit removal.

SUMMARY

A conceptual model has been proposed to describe the interrelationship between biofouling and corrosion in a Cu-Ni alloy. Laboratory results have been presented which are consistent with the proposed model. The experimental results suggest several mechanistic hypotheses requiring further experimental testing which is currently underway.

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